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 TI Copper alloys as silver-solder substitutes and their manufacture  
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AB The Ag-solder substitutes have chemical compns. as follows: (1) low-temperature solders containing Sn 3-10, Zr 0.02-0.20, P 3-10, Ti 0.02-0.20, Ni 0.5-15, Ce 0.01-0.05, Si 0.05-0.20% and balance Cu; or (2) middle-temperature solders containing Sn 3-10, Zr 0.02-0.20, P 0.02-0.20, Ti 0.02-0.20, Ni 0.5-15, Ce 0.01-0.05, Si 0.05-0.20, Zn 20-45% and balance Cu. The Ag-solder substitutes are manufactured by cutting raw materials to small lumps, pickling, adding to graphite crucible, melting with sonic wave energy, sucking to form soldering rods, or casting to form ingots followed by processing to form strips or powder.

PTO 2008 - 7132

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Application No. 91103137, filed May 12, 1991; Inventor: FENG, Jinling. Assignee: FENG, Jinling

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SILVER SUBSTITUTE WELDING COMPOUND AND MANUFACTURE METHOD

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[54] [Name of Invention] Silver Substitute Welding Compound and Manufacture Method

CLAIMS

1. The silver substitute welding compound concerns a welding compound; the raw materials include Cu, P, Sn, Ni and it is characterized in that it also includes Zr, Ce, Ti, and Si that have an activating effect, and sometimes it also includes Zn that has an activating effect too; the chemical composition of this low-temperature welding compound is (in weight %) 3 – 10% Sn, 0.02 – 0.20% Zr, 3 – 10% P, 0.02 – 0.20% Ti, 0.5 – 15% Ni, 0.01 – 0.05% Ce, 0.05 – 0.20% Si, and the rest is Cu; the chemical composition of this medium-temperature welding compound is (in weight %) 3 – 10% Sn, 0.02 – 0.20% Zr, 0.02 – 0.20% P, 0.02 – 0.20% Ti, 0.5 – 15% Ni, 0.01 – 0.05% Ce, 0.05 – 0.20% Si, 20 – 45% Zn, and the rest is Cu.
2. The manufacture method of silver substitute welding compound concerns the preparation of the welding compound; its operations include turning the raw material into small pieces with sheet metal shears or a cutter and washing it clean with an acid; putting together a batch as needed, placing it into the graphite crucible (10) on the smelting furnace and smelting until completely molten, removing surface impurities, and then casting it into ingots, followed by machining it into thin strips welding compound or powdered welding compound, and it is characterized in that during the smelting, when all of the raw material is molten, a sound wave generator (1) and a vibration system are used to generate sound wave energy for 5 to 10 minutes that can introduce complete osmosis of individual melt components and the forming of a eutecticum, effective removal of impurities and gas; the vibration system consists of a power transformer (6) and an amplitude modulating pole (7). The transformer (6) is composed of a square laminate with a rectangular slot in it punched by the oxidation processing of a nickel cover; on two sides it has 15 -20 windings of conducting wire; the amplitude modulating pole (7) is a cascade-shaped cylinder made of steel No. 45 whose thick end's top surface is welded together with the bottom end surface of the power transformer (6).
3. The manufacture method of silver substitute welding compound under Claim 2 characterized in that the machining of the thin strip welding compound is performed by placing the cast ingot on a mechanical slicer and mechanically slicing.
4. The manufacture method of silver substitute welding compound under Claim 2 characterized in that the machining of the welding rod is performed after the raw material undergoes the introduction of sound wave power smelting, without casting, but while maintaining the molten state; the melt that was preheated to 200°C by baking and had a heat-resistant tube (13) of the vacuum system (11) directly inserted into it is lifted immediately after suction and placed into water for quick cooling; the heat-resistant tube

(13) can be made of industrial glass, quartz glass, ceramics or graphite, and its inner diameter is the requisite diameter of the welding rod.

## SPECIFICATION

### Silver Substitute Welding compound and its Manufacture Method

The silver substitute welding compound and manufacturing method concern welding compound and manufacture method.

Silver is a precious and important metal that is in short supply in the world. Silver consumption has grown continuously with the development of industry, and the world's silver deposits are continuously being depleted, which has an impact on the existence and development of industries that use silver. The silver welding compound of Prior Art has the following two drawbacks. The first one involves the ready vaporization of silver during welding in the event of high pressure of silver vapor, which causes electrical leakage and sparking, adversely affecting the product's performance as an electrical appliance. For example, a powerful transistor is the heart of a set, but a silver welding compound connection is utilized in its substrate. Silver vaporization diminishes the resistance of the substrate insulation and thus affects the transistor's performance. The second one involves the readily induced fusion, scorching and fracturing of the welded material in the event of an excessive osmosis intensity of silver affecting the product's air tightness and durability, for example, electric vacuum devices. Therefore, people have been continuously searching for a non-silver welding compound to substitute for silver. Current domestic and foreign formulations for silver substitute welding compound consist of four materials Cu, P, Sn and Ni. The materials are smelted mostly by smelting in the air, (coke and resistance heating as well as induction heating) or by more advanced vacuum smelting (induction heating, therefore, the smelting materials contain lots of gas leading to boiling phenomenon during welding and causing the welding compound to spurt to non-welded surface, bringing about electrical leakage of the product, sparking or blasting and affecting the product's airtight characteristics. A real eutectic cannot be formed among the multiple raw materials of the welding compound, therefore there is large free flowing property and a significant weakening of the joint filling capacity; there is a lot of impurities in the welding joint, which affects not only the air tightness of the product joints but also can easily produce electrical leakage, sparking and coarsening of the crystal grains in the welding compound, reducing mechanical characteristics of the welded product such that it may easily crack from thermal shock and bringing down the reliability of the product. Currently roll compacting is used for the processing of all strip material, compacting it from a cast ingot into roughly 0.15 mm thick strips that are currently in common use. This takes several dozens repeat cycles of rolling and annealing, during which impurities are readily introduced, and the material is also apt to become oxidized; this is particularly true of the silver substitute material whose raw materials are brittle to begin with, such that hot compression must be used and oxidation is even more serious; in addition the amount that is compressed down each time is very small, and the productivity is quite low. A number of initial and finishing rolling mills must be prepared as well as a number of annealing furnaces and auxiliary equipment (such as precision grinders), therefore substantial capital investments are required. For example, the use of the most recently successfully researched technology of producing non-crystalline thin strips by fast rejection has the drawback that the machined thickness can be only thinner than 0.04 mm (but weldment require that the thickness of the welding compound be between 0.1 ~ 0.15 mm), moreover, large investments are needed and the

cost is high. Currently for wire (that is, welding rods) machining, rolling and drawing are commonly used, but since hot rolling and hot drawing are used, the material is readily oxidized and impurities are readily introduced, which affects the welding rod's quality, and since repeat cycles of rolling and annealing are required the efficiency is low.

The purpose of this invention is to offer a silver substitute welding compound and its manufacture method whose characteristics are superior to those currently available and which is capable of substantially increasing the production efficiency and reducing production costs.

The silver substitute welding compound of this invention apart from including as raw materials Cu, P, Sn, Ni, also includes Zr, Ce, Ti, and Si that have an activating effect, and sometimes it also includes Zn that has an activating effect too; the chemical composition of this low-temperature welding compound is (in weight %) 3 – 10% Sn, 0.02 – 0.20% Zr, 3 – 10% P, 0.02 – 0.20% Ti, 0.5 – 15% Ni, 0.01 – 0.05% Ce, 0.05 – 0.20% Si, and the rest is Cu; the chemical composition of this medium-temperature welding compound is (in weight %) 3 – 10% Sn, 0.02 – 0.20% Zr, 0.02 – 0.20% P, 0.02 – 0.20% Ti, 0.5 – 15% Ni, 0.01 – 0.05% Ce, 0.05 – 0.20% Si, 20 – 45% Zn, and the rest is Cu.

The manufacture method of this invention includes turning the raw material into small pieces with sheet metal shears or a cutter and washing it clean with an acid (it could be nitric acid, hydrochloric acid or chromic acid); putting together a batch as needed, placing it into the graphite crucible (10) on the smelting furnace and smelting until completely molten, introducing a sound wave generator (1) and a vibration system are used to generate sound wave energy for 5 to 10 minutes that can introduce complete osmosis of individual melt components and the forming of a eutecticum, effective removal of impurities and gas followed by removing surface impurities, and casting ingots, with subsequent machining into thin strips welding compound or powdered welding compound. The vibration system consists of a power transformer (6) and an amplitude modulating pole (7). The transformer (6) is composed of a square laminate with a rectangular slot in it punched by the oxidation processing of a nickel cover; on two sides it has 15 -20 windings of conducting wire; the amplitude modulating pole (7) is a cascade-shaped cylinder made of steel No. 45 whose thick end's top surface is welded together with the bottom end surface of the power transformer (6). The machining of the thin strip of the welding compound of this invention is performed by placing the cast ingot on a mechanical slicer and mechanically slicing it once according to the required thickness and width. The processing of the powdered welding compound is performed by placing the cast round ingots on the lathe and lathing into fragments or placing the cast square ingot on a slicer and slicing into fragments. Then the fragments are placed into a high speed rotary pulverizer and pulverized; the resulting powder is strained to produce powdered welding compound. The processing of the welding rod is performed as follows: after the raw material undergoes the introduction of sound wave power smelting, without casting, but while maintaining the molten state; the melt that was preheated to 200°C by baking and had a heat-resistant tube (13) of the vacuum system (11) directly inserted into it is lifted immediately after suction and placed into water for quick cooling; the heat-resistant tube (13) can be made of industrial glass, quartz glass, ceramics or graphite, and its inner diameter is the requisite diameter of the welding rod.

Fig. 1 is the diagram of the raw material smelting. 1 is a sound wave generator, 2 is a sound wave output conducting wire, 2 and 8 are the transformer cooling water systems, 4 is a support frame, 5 is the transformer cooling jacket, 6 is the transformer, 7 is the amplitude modulating pole, 9 is the molten metal, 10 is the crucible.

Fig. 2 is the diagram of a welding rod made by vacuum suction. In the Figure, 10 is the crucible, 11 is the vacuum system, 13 is the heat resistant tube, 14 is the soft tube, 15 is the switch.

Fig. 3 is the diagram of a nickel piece used for the transformer, after punching.

Fig. 4 is the diagram of the amplitude modulating pole.

The following is an embodiment of this invention. First, a vibration system was made; pieces of nickel that were 0.1 mm thick were oxidized and then, as shown in Fig. 3, made into thin pieces that were 110 mm long and 70 mm wide with a 10 mm x 70 mm slot punched in the middle; they then were stacked to a thickness of 40 mm, and 15 windings of conducting wire were wound over the two longer sides, rendering it into a transformer. No. 45 round steel was made into a cascade shaped cylinder, the diameter of its thicker end was 60 mm, its length was 60 mm and the diameter of the thinner end was 25 mm, while its length was 180 mm and a welding rod was prepared, whereupon the top face portion of its thick end was welded together with the bottom face of the transformer, thus completing a vibration system. Ti, Ni, Ce, Si, Zr, Sn, a P-Cu alloy, and electrolytic Cu<sup>1</sup> were cut up into small pieces with plate shears and washed clean with hydrochloric acid. Then 0.7 kg Sn, 0.007 kg Zr, 0.007 kg Ti, 0.07 kg Ni, 0.0035 kg Ce, 0.0035 kg Si, 1.62 kg P – Cu alloy (P content 13%), and 4.59 kg electrolytic Cu were weighed and put aside. A coke furnace was fired and a graphite crucible full of charcoal dust (acting as the reducing agent) was placed on the furnace for baking and gas removal. A number 10 graphite crucible for melting was also placed on the furnace for baking and gas removal. When its internal walls turned red, the above-mentioned weighed raw materials were placed into the crucible one by one in a sequence of steps, starting with P – Cu alloy. At the same time the small pieces of Cu and Ni were placed on the furnace floor for preheating. As soon as the P – Cu alloy was molten, the preheated electrolytic Cu and Ni were immediately placed into the crucible, and a ladle was used to cover the surface with charcoal dust, and the crucible was covered with a lid. An air blower was started to raise the temperature and the cooling water of the sound wave vibration system was turned on, as was the low pressure switch of the sound wave generator. As soon as the electrolytic Cu and Ni were completely molten, they were stirred for 1 – 2 minutes with a graphite rod that had undergone baking, then Sn was added and stirred for 0.5 min, then Zr, Ti, and Ce were added and stirred for another 0.5 min. The frame used to suspend the vibration system was shifted such that the small head end of the amplitude modulating pole was placed on the furnace for baking for 2 min., and the frame was moved again such that the small head end of the vibration system at a depth of 10 mm from the melt in the furnace. The sound wave generator's high pressure switch was immediately turned on, such that the sound wave generator was outputting sound energy. Moreover, the vibration

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<sup>1</sup> Sic! – translator's note

system was introduced into the melt and kept there for 5 minutes, whereupon the generator's power was cut off and the vibrator system was moved away. Surface impurities were removed from the melt surface with a ladle, and the crucible was removed to a casting platform by holding it securely with tongs. Casting was performed aiming for a pre-baked die. Casting was immediately followed with cooling with tap water, and after the cooling a cast ingot was removed. The cast ingot (square ingot) was placed on a slicer and sliced into welding compound in the shape of strips to meet the requirement of 10 · 15 mm thick and 10 mm wide. These welding compound strips are the low temperature welding compound.

In another embodiment of this invention, a medium temperature welding compound was prepared (the vibration system was made in the same way as in the above-mentioned embodiment.) Ti, Ni, Ce, Si, Zr, Sn, Zn, a P-Cu alloy (P content 13%), and electrolytic Cu were cut up into small pieces with a cutter and washed clean with nitric acid. Then 0.49 kg Sn, 0.007 kg Zr, 2.1 kg Zn, 0.007 kg Ti, 0.07 kg Ni, 4.3 kg Cu, 0.0035 kg Ce, 0.0035 kg Si, 0.028 kg P – Cu alloy, and 4.59 kg electrolytic Cu were weighed and put aside. A coke furnace was fired and a graphite crucible full of charcoal dust (acting as the reducing agent) was placed on the furnace for baking and gas removal. A number 10 graphite crucible for melting was also placed on the furnace for baking and gas removal. When its internal walls turned red, the above-mentioned weighed raw materials were placed into the crucible one by one in a sequence of steps, starting with P – Cu alloy. At the same time the small pieces of Cu and Ni were placed on the furnace floor for preheating. As soon as the P – Cu alloy was molten, the preheated electrolytic Cu and Ni were immediately placed into the crucible, and a ladle was used to cover the surface with charcoal dust, and the crucible was covered with a lid. An air blower was started to raise the temperature and the cooling water of the sound wave vibration system was turned on, as was the low pressure switch of the sound wave generator. As soon as the electrolytic Cu and Ni were completely molten, they were stirred for 1 – 2 minutes with a graphite rod that had undergone baking, then Sn was added and stirred for 0.5 min, then Zr, Ti, and Ce were added and stirred for another 0.5 min. The frame used to suspend the vibration system was shifted such that the small head end of the amplitude modulating pole was placed on the furnace for baking for 2 min., and the frame was moved again such that the small head end of the vibration system was at a depth of 10 mm from the melt in the furnace. The sound wave generator's high pressure switch was immediately turned on, and remained so for 5 minutes, whereupon the generator's power was cut off and the vibrator system was moved away. Surface impurities were removed from the melt surface with a ladle. The crucible was secured with tongs and placed on a platform. A glass tube made of industrial glass with an internal diameter of 4 mm that had been pre-selected and preheated in a dry oven to a temperature of 200°C was removed and inserted into one end of a soft tube connected to a mechanical vacuum pump. The pump was connected to a power source and the glass tube's end was immersed into the melt. As soon as the melt was suctioned into the glass tube, the glass tube was immediately placed in a cooling water container that was provided nearby, thus yielding a welding rod. Suction was performed with another glass tube and the operation was repeated.

The welding compound manufactured according to the formulation and the method of this invention is of good quality, has no impurities, is not readily oxidized; furthermore, it offers high productivity, low cost, lack of restrictions on the thickness of the thin strip

welding compounds. The welding compound of this invention can be used wherever silver welding compounds must be used. The smelting method of this invention is superior to the best vacuum smelting currently available in industry because it has the characteristic features of better smelting quality, lower cost, higher efficiency and lower investments. It is suitable for small batch research and experimental applications while being suitable also for large-scale production. It is suitable for the smelting of both non-silver welding compound and silver welding compound, as well as for the smelting of various high-grade non-smelting compounds. The machining methods of the thin strip welding compound of this invention are suitable for the machining of thin strips made of different compounds including welding compounds; moreover, they have the advantage of producing a lot of quality product fast and economically. The welding rod machining methods can manifest even further superiority in being suitable for various materials, in particular, for materials that are highly brittle and hard to machine by regular methods.

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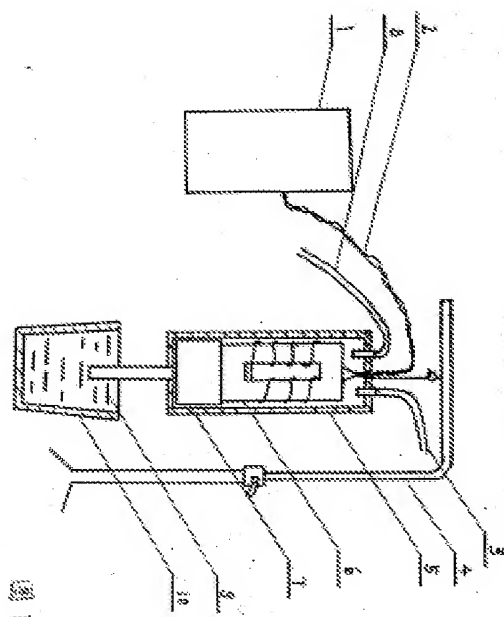


图 1

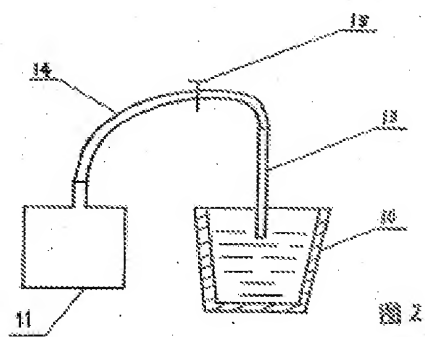


图 2



图 3

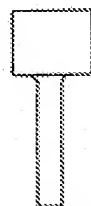


图 4